Art. XVI.—*The Oxidation of Cane Sugar by Aqueous Solutions of Potassium Permanganate.*

(With Plates XXI., XXII.)

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[Read 8th December, 1898].

The *Dictionnaire de Chemie* states that sugar is oxidised entirely to carbonic acid and water by permanganate of potash in an acid solution.
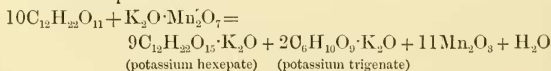
Watt's Dictionary says that sucrose is easily oxidised by all ordinary oxidising agents and that $KMnO_4$ is *said* to yield CO_2 and H_2O; but that Liebig and Pelouze had found that oxalic acid was produced unless an excess of $KMnO_4$ were present, in which case carbonates were formed.

But the accuracy of these statements has been called in question, and at the suggestion of Professor Masson, this research has been undertaken with the view of testing their validity.

It may be observed, however, that the action has not been wholly overlooked, and those chemists who have investigated the subject have found, speaking generally, that the sugar molecule is broken up into molecules of smaller carbon content; oxalates, formates, carbonates and salts of other acids being formed under varying conditions; but considerable differences of opinion prevail as to the manner in which the permanganate is reduced.

Literature of Sugar Oxidation.

Maumené (*Compt. Rend.*, 75, p. 85) gives this equation as the result of his experiments :—

$$10C_{12}H_{22}O_{11} + K_2O \cdot Mn_2^{'}O_7 =$$
$$9C_{12}H_{22}O_{15} \cdot K_2O + 2C_6H_{10}O_9 \cdot K_2O + 11Mn_2O_3 + H_2O$$

(potassium hexepate)   (potassium trigenate)

He dissolved

200 grammes of sugar-candy in 2 litres of water, and

200 grammes of potassium permanganate in 4 litres of water. These solutions were then mixed and stirred. The temperature rose 20°C. and the liquid gelatinized. The filtrate was neutral; and on the strength of a few qualitative tests he claimed the discovery of these two new acids.

The latter name, "trigenic," had, however, been applied by Liebig and Wöhler before the year 1850 (*Annalen*, 59, p. 296), to an entirely different compound, $C_4H_7N_3O_2$, which is also known as ethylidene biuret.

In a later paper (*Compt. Rend.*, 120, p. 783) he says that if the precipitated oxide, which is either Mn_2O_3, or a mixture of MnO_2 and MnO, be kept for several days in contact with a strong solution of sugar the brown colour will disappear and hexepic acid ($C_6H_{12}O_8$) be produced. But he explains the failure of other chemists to obtain these acids by the fact that if excess of Mn_2O_3 be present then in time they become further oxidised to form lactic and formic acids.

Heyer (*Arch. Pharm.* [3] 20, p. 430, and *Chem. Soc. abstracts*, 1882, p. 1041) has repeated the experiments of Maumené and other observers. He also employed strong solutions and found that one equivalent of sugar does not react completely in the cold with 4 equivalents of $KMnO_4$, oxalates and formates being obtained; if 12 equivalents of $KMnO_4$ be employed then formates and carbonates, but no oxalates are formed.

$$C_{12}H_{22}O_{11} + 12KMnO_4 = 6KHCO_3 + 6KHCO_2 + 12MnO_2 + 5H_2O.$$
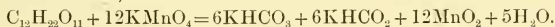
He says that Maumené's "hexepate" was really oxalate, and his "trigenate" was possibly a mixture of acetates and formates of potassium.

Heyer also repeated Langbien's experiments and found that sulphuric acid intensified the reaction; whilst if sufficient acid were present, then a manganese salt, and not one of the oxides, was produced. Also the higher the temperature and the greater the amount of $KMnO_4$ present, the more sugar is completely oxidised to carbonate.

Laubenheimer (*Chem. Soc. abstracts*, 1873, p. 46) obtains a similar result for the oxidation of *Lactose* by warm alkaline solutions of permanganate—CO_2 and MnO_2 being the products.

Smolka (*Monatsh. Chem.* 8, p. 1, and *Chem. Soc. abstracts*, 1887, p. 566) finds that when *Dextrose* is boiled with excess of $KMnO_4$ it is completely oxidised thus :—

$$C_6H_{12}O_6 + 8KMnO_4 = 2KH_3Mn_4O_{10} + 3K_2CO_3 + 3CO_2 + 3H_2O$$

the MnO_2 being in combination with some of the K_2O to form a *potassium hydro-manganite* ($K_2O \cdot 3H_2O \cdot 8MnO_2$).

The amount of oxidation varies with the temperature and concentration of the solution and if there be not excess of $KMnO_4$ present, oxalates, formates and unaltered dextrose, result; whilst the $KMnO_4$ is reduced partly to manga*nic* and partly to manga*nous* oxides.

It is obvious that cane sugar would be largely converted into dextrose and laevulose by heating in dilute acid solutions.

Morawski and Stingl (*Journ. der prakt. Chem.* [2] 18, p. 78) find that $KMnO_4$ on reduction in neutral or alkaline solutions with oxalic acid among other reducing agents produces a brown precipitate of $KH_3Mn_4O_{10}$, *i.e.* a salt of tetramanganic acid. They also give a theory of the constitution of $KMnO_4$ and its reduction products.

Feilitzen and Tollens (*Berichte*, 1897, p. 2581) took strong solutions of $KMnO_4$ and sugar containing about 5 equivalents of $KMnO_4$ to one of sugar and left them after mixing until the next day.

The precipitate obtained was thoroughly washed (with alcohol towards the end of the operation), dried, and then analysed with the following result :—

		Percentage Composition.			Chemical Equivalents.
Mn_2O_3	$=$	83·34	·	·	10·32
K_2O	$=$	9·48	·	·	2·0
C	$=$	0·60	·	·	1·0
H_2O	$=$	8·37	·	·	9·2

100·79

The amount of carbon was found to vary from 8·5% to 1·6% to 0·6% according to the amount of washing, and was probably due to the presence of some unoxidised sugar.

It will be noted that the precipitate was found to be Mn_2O_3 and not MnO_2.

The K_2O was evidently, partly at all events, in combination with the Mn_2O_3, for it is difficult to understand how so much alkali could have remained merely *adsorbed* after the long continued washing to which it had been subjected.

Preliminary Experiments and Theory of Action.

Test tube experiments shewed that sugar solutions stronger than about ten per cent. readily acted on approximately saturated solutions (6·25 per cent.) of potassium permanganate, either on leaving to stand for a short time or immediately on heating to about 30°C. ; in both cases the whole mixture gelatinized, evidently in consequence of the precipitation of a hydrated oxide of manganese. With weaker solutions a higher temperature was required, and the reaction was slower and less energetic, no gelatinization taking place though a precipitate was still formed. The presence of acids such as acetic, hydrochloric and sulphuric, considerably accelerated the action.

With the object of determining the oxidation products of the sugar, I took solutions of about four per cent. strength, and mixed them in the ratio of one molecule of sugar to 4 molecules of $KMnO_4$ approximately. After boiling and filtering from the precipitated oxide, the solution was neutral to litmus, and effervesced with dilute acids, and gave a white precipitate with silver nitrate, soluble in acetic and other dilute acids, and which blackened on heating. No precipitate was obtained with calcium chloride in presence of dilute acetic acid.

These tests indicated the presence of carbonates and formates, and shewed the absence of oxalates.

Possibilities open for the Reaction according to Chemical Theory :

A. OXIDATION OF THE SUGAR.

(i.) *Complete Oxidation :*—to *carbonic acid* and water, each sugar molecule requiring 24 atoms of Oxygen. $C_{12}H_{22}O_{11} + 24O = 12CO_2 + 11H_2O$.

(ii.) *Partial Oxidation :*—to *oxalic acid* and water, each sugar molecule requiring 18 atoms of oxygen. $C_{12}H_{22}O_{11} + 18O = 6H_2C_2O_4 + 5H_2O$.

(iii.) *Partial Oxidation :*—to *formic acid*, each sugar molecule requiring 12 atoms of oxygen. $C_{12}H_{22}O_{11} + H_2O + 12O = 12CH_2O_2$.

B. Reduction of the Potassium Permanganate to supply the oxygen necessary for the oxidation of the sugar may also be to one of several conditions.

> (i.)   *Manganese peroxide :*—MnO_2.
> (ii.) *Manganic oxide :*—Mn_2O_3.
> (iii.) *Manganous oxide :*—MnO (in form of a manganous salt if in presence of acid).
> (iv.) A *variable mixture* of MnO_2, Mn_2O_3 and MnO.

The amounts of oxygen liberated in cases (i.), (ii.) and (iii.), from two molecules of $KMnO_4$ is shewn thus :—

> (i.) $2KMnO_4 = 2MnO_2 + K_2O + 3O$.
> (ii.) $2KMnO_4 = Mn_2O_3 + K_2O + 4O$.
> (iii.) $2KMnO_4 = 2MnO + K_2O + 5O$.

In the case of the sugar being all completely oxidised to carbonic acid, as seems probable, and supposing the $KMnO_4$ to be all reduced to one only of these three conditions, then the number of molecules of $KMnO_4$ required for the oxidation of each sugar molecule will be :—

> (1) 16 :—if MnO_2 be formed.
> (2) 12 :—if Mn_2O_3 be formed.
> (3) 9·6 :—if MnO be formed.

In the possible case of formates or oxalates being produced in the reaction, one half or three quarters of these amounts of $KMnO_4$ would be required.

Preliminary experiments with dilute solutions $\left(\dfrac{N}{500}\right.$ Sugar and $\dfrac{N}{50}KMnO_4\Big)$ shewed that up to 16 equivalents (molecules) of $KMnO_4$, may be decolorised for each equivalent of sugar in presence of dilute sulphuric acid.

In these cases most, if not all of the sugar must have been oxidised to CO_2 and H_2O, and most, if not all of the $KMnO_4$ must have been reduced only to MnO_2.

The action may be tentatively represented as taking place according to this equation if in neutral solution :—

$$C_{12}H_{22}O_{11} + 16KMnO_4 = 8K_2O + 16MnO_2 + 12CO_2 + 11H_2O.$$
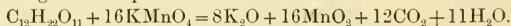
We must bear in mind, however, that the K_2O is probably in combination with both the MnO_2 (Smolka, *loc. cit.*, and Morawski

and Stingl, *loc. cit.*) and the CO_2 for the filtrate is neutral to litmus, and effervesces with dilute acids.

If in presence of free acid, this uncertainty does not exist, and as the precipitated MnO_2 is insoluble in dilute sulphuric acid, we may write as the final result of the oxidation of the sugar by acid solutions of permanganate,

$$C_{12}H_{22}O_{11} + 16\,KMnO_4 + 8\,H_2SO_4 = 8\,K_2SO_4 + 16\,MnO_2 + 12\,CO_2 + 19\,H_2O.$$
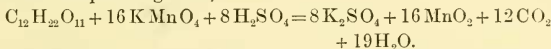
As, however, we get MnO_2 formed in presence of $KMnO_4$ especially when excess of the latter is used, it is necessary to take account of any possible interaction between them.

Literature of Secondary Reaction.

Morse, Hopkins and Walker (*Am. Chem. Journ.*, 18, p. 401) have shewn that under similar conditions MnO_2 is capable of reducing $KMnO_4$ with liberation of free oxygen. Thenard noticed and commented on this reducing action in 1856.

After pointing out that the stability or otherwise of different samples of "permanganate solutions" is due to the absence or presence of this manganese peroxide, they describe an experiment in which half of the manganese in a measured quantity of $KMnO_4$ is precipitated as MnO_2 by the calculated amount of manganese sulphate and the flask containing the solution immersed in boiling water. After some time the pink colour of $KMnO_4$ will have disappeared altogether. The amount of "active oxygen" remaining, shows that all the manganese is present as MnO_2 and measurement of the oxygen evolved confirms this.

They give this equation as representing the reaction.

$$2\,HMnO_4 + MnO_2 = H_2O + 3\,MnO_2 + 3O.$$
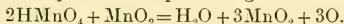
The oxide resulting from complete reduction of a neutral solution of $KMnO_4$ contains all the potassium of the original salt and the supernatant liquid is therefore neutral and gives practically no deposit on evaporation.

Unless excess of $KMnO_4$ be present, the precipitated oxide loses oxygen even at ordinary temperatures, so that if it be first dried, or the analysis be delayed for a few hours, then the proportion of oxygen to manganese will be smaller than will satisfy the formula MnO_2.

Possibly this may account for Maumené, Feilitzen and Tollens and others obtaining results indicating that Mn_2O_3 and not MnO_2 is precipitated by sugar from solutions of $KMnO_4$.

Morse and Reese (*Am. Chem. Journ.*, 20, July) contend that the evolution of oxygen observable in most cases where $KMnO_4$ is reduced to MnO_2 is due to this action of the precipitated peroxide on the excess of $KMnO_4$.

Jones (*Journ. Chem. Soc.*, 1878, p. 95), Tivoli (1890) and Gorgen (*Compt. Rend.*, 110, p. 958) have examined the action of various reducing agents on $KMnO_4$, and obtained results confirming this opinion.

Two German Chemists, Meyer and Recklinghausen (*Berichte d. Chem. Ges.*, 29, p. 2828), found that when Hydrogen or Carbon monoxide was absorbed by strong solutions of $KMnO_4$ oxygen was evolved and MnO_2 precipitated ; but they argue that this liberation of oxygen was not due to the action of MnO_2 on $KMnO_4$, as the evolution took place mainly, and in some experiments entirely, whilst the Hydrogen on carbon monoxide was being absorbed by the solution.

Further evidence has been produced on both sides, but so far the question can hardly be regarded as settled either one way or the other.

However, it will certainly be necessary to bear this secondary action in mind whilst examining the oxidation of cane sugar.

Experimental Part.

(a) *Objects aimed at.*

The preliminary experiments previously described having approximately shewn that each molecule of sugar requires 16 molecules of $KMnO_4$, at least under certain circumstances, my attention has been directed towards ascertaining under exactly what conditions this complete oxidation of the sugar takes place, and investigating the nature and extent of any secondary reactions or other modifying influences.

To do this it was necessary to determine by series of experiments the effect of varying

(i.) the *ratio* of the sugar, acid and permanganate to one another,

(ii.) the *concentration* of the solutions,

(iii.) the *temperature* of experiment,

(iv.) the *time* of the experiment,

and finally, to decide what was the shortest time in which the reaction could be made to complete itself under suitable and convenient conditions.

(b) *Experimental Methods.*

An attempt was made to titrate a known amount of sugar with a standard solution of $KMnO_4$.

Sugar solutions, even if very dilute, were found in the presence of dilute acids (sulphuric was used) to readily reduce, *i.e.*, decolorize, a few drops of $\frac{N}{50}$ $KMnO_4$ solution, on boiling.

But when about 1·75ccs. $\frac{N}{50}$ $KMnO_4$ had been added in this way to 10ccs. of $\frac{N}{1000}$ Sugar solution in a flask, the brown precipitate which was formed would no longer dissolve, and after nearly 5ccs. of the permanganate solution had been added, its pink colour permanently remained even on continued boiling. Excess of acid did not influence this result.

Nearly 10 equivalents of $KMnO_4$ had been added to each equivalent of sugar, but as 9·6 $KMnO_4$ is required for complete oxidation of sugar, if itself entirely reduced to $MnSO_4$ as apparently was only the case at first, then all the sugar could not have been oxidised to carbonic acid, and probably some was only oxidised to the condition of oxalic or formic acids, or a still lower state of oxidation.

Direct titration not being possible, it was evident that practically only three methods of following the course of the reaction were available.

(i.) Estimation of the carbonic acid, produced by the oxidation of a known weight of sugar, by absorption in soda-lime tubes or otherwise, as in organic analysis.

(ii.) Some modification of the "Forchammer" or "Oxygen" process, which is used for estimating organic matter in potable and other waters.

> (iii.) Estimation (volumetrically) of the amount of manganese peroxide precipitated.

The first was not made use of, as the volumetric method, besides being quicker, would give quite as accurate results with the dilute solutions employed.

The method of conducting the experiments was as follows :—

Generally 50ccs. $\frac{N}{50}$ KMnO$_4$ and 5·30ccs. $\frac{N}{500}$ sugar were used, and the desired amount of $\frac{N}{2}$H$_2$SO$_4$ added to the same flask. The flask was now heated for the time required at some particular temperature and then rapidly cooled.

The solution could now be filtered through asbestos and the "active oxygen" in either the filtrate or the precipitate or both, estimated by titration with a standard solution of ferrous ammonium sulphate.

In some experiments the solution was not filtered and the total "active oxygen" remaining in the liquid determined in the same way.

The ferrous solution mentioned contained about two equivalents of free sulphuric acid to each equivalent of the salt, in order to render it capable of readily dissolving manganese oxides, and is subsequently denoted by [Fe].

It was soon evident that, to obtain accuracy, attention must be paid to

> 1 Purity and exact standardization of reagents.
> 2 Careful regulation of the duration and temperature of experiments.

1. The reagents employed were

> (i.) Cane Sugar :—
>> Ordinary white "brewer's crystals" were used as being almost chemically pure.
>>
>> At first trouble was experienced with an organic growth in the dilute solutions used ; this was effectually prevented by previously rinsing out the well-stoppered bottle with mercuric chloride.

(ii.) Potassium permanganate :—

As the solutions under ordinary circumstances are so unstable, the ordinary pure salt was used, and the solution constantly restandardized with pure iron wire or recrystallized ferrous ammonium sulphate.

(iii.) Ferrous ammonium sulphate :—

The salt obtainable was in obviously impure crystals ; some was recrystallised for use as a standard and found to compare satisfactorily with pure iron wire.

A larger quantity was purified by precipitation with alcohol ; by this means the salt was obtained in a readily soluble powder, which was of about 99 per cent. purity. This was of no consequence, however, for the solution required restandardizing every two or three days.

(iv). A semi-normal sulphuric acid was employed and prepared from the ordinary laboratory reagents.

2. The contents of the flask in which the experiment was conducted were quickly heated by immersing in water a few degrees hotter than the desired temperature and cooled at the conclusion of the experiment in cold water.

In this way an uncertainty of not more than one minute was introduced, and where the experiment continues for an hour or over, this is negligible.

Keeping the temperature constant to within 1°C. is however a more serious consideration.

For temperatures below 100°C. the liquid was contained in ordinary stoppered 100cc. flasks which were allowed to rest on a perforated shelf in a large constant level water-bath. The water was kept at the desired temperature by heating with a bunsen burner.

In my later experiments on the velocity of the reaction efficient circulation of the water was produced by means of a central vertical cylinder surrounding a screw propeller worked by a small water motor.

The temperature was more exactly regulated by a vapour pressure thermostat and the effect of air currents minimised by the use of separate covers fitting over the neck of each flask.

The circulation of the water takes place in a uniform manner, the current passing up through the central cylinder from directly over the flame, and it then spreads out across the shelf and around the flasks and thermostat, and finally down the sides through openings for that purpose.

The result is that a thermometer with the bulb placed in any part of the vessel shews readings not differing by more than 1°C., and if kept in the region of the flasks, this difference practically vanishes.

Where 100°C. was the temperature desired, the flask was simply placed on a sand bath, so heated that the liquid was just kept in a state of quiet ebullition.

(c) *Calculation of Results.*

In the titration of the amount of reduction undergone by the $KMnO_4$ in any experiment, one or more of three methods was employed.

1. Estimation of the amount of *MnO_2 precipitated* by complete filtration of the solution through asbestos, and washing of the precipitate until no pink colour of $KMnO_4$ remained.

This precipitate was then *at once* dissolved in excess of $\frac{N}{10}$ or $\frac{N}{50}$ [Fe] and then the excess determined by titration with $\frac{N}{50} KMnO_4$.

2. Estimation of the *$KMnO_4$ reduced* to MnO_2; this was done in either of two ways.

(i.) The liquid and precipitate was made up to 100ccs., and then *part* of it filtered into a burette and titrated against a fixed volume of [Fe].

A simple calculation gives the amount of $KMnO_4$ reduced to MnO_2, and this method was employed in the majority of my earlier experiments.

Thus in experiment 2 of Table II., it was found that 14·4ccs. of the filtered solution were

required to produce a pink coloration in 5ccs. $\frac{N}{10}$ [Fe].

but as 5ccs. $\frac{N}{10}$ [Fe] is equivalent to (will combine with) 1cc. $\frac{N}{10}KMnO_4$.

14·4ccs. of the filtered solution contained as much $KMnO_4$ as 10ccs. $\frac{N}{100}KMnO_4$.

$\therefore$ 100ccs. contained $\frac{1000}{14·4}$ccs., $\frac{N}{100}KMnO_4$

$$= 69·44\text{ccs. } \frac{N}{100}KMnO_4.$$

and $100 - 69·44$ (*i.e.*, 30·56) $\frac{1}{100}$-milligram molecules of $KMnO_4$ have been reduced to MnO_2.

(ii.) By complete filtration of all solution and separation of all MnO_2.

The filtrate and washings were then made up to 100ccs. and their value estimated as in (2) (i.), or the whole may be neutralised with excess of ferrous solution as in (1).

The precipitated MnO_2 can also be estimated by (1). The objection to (i.) is that the volume of the precipitated MnO_2 is not allowed for, and adsorbtion may also exercise an effect on the result. Probably both sources of error are negligible, especially as they tend to neutralize one another.

The disadvantage of (ii.) is that it involves the complete filtration of the whole of the solution and thorough washing of the precipitate; operations which occasionally (when the asbestos filter becomes clogged) may be very tedious.

3. Estimation of the *total loss* of "*active oxygen*" in the liquid.

> (i.) This may be calculated from 1 and 2 (ii. combined). The concordance of the results so obtained is a useful check on the accuracy of the work.
>
> (ii.) It may also be determined directly by adding excess of ferrous solution directly to the liquid and then titrating back with standard $KMnO_4$ in the usual way.
>
>> This method is superior to the others, both in point of accuracy and of speed when only a small amount of MnO_2 has been precipitated, for then 50ccs. of $\frac{N}{10}$ [Fe.] (equivalent to the 50ccs. of $\frac{N}{50}KMnO_4$ originally present) can be directly added, the same pipette being used for the measurement of both solutions, and the excess of ferrous salt readily determined by titration with $\frac{N}{50}KMnO_4$.

(d) *Explanation of tables of results.*

The columns indicating the time and temperature of experiments and the amounts of $\frac{N}{50}KMnO_4$, $\frac{N}{500}$ sugar and the amounts $\frac{N}{2}H_2SO_4$ do not need further elucidation.

The results of the titrations have been given in one of three columns according to the method of estimation.

> α. The amount of *$KMnO_4$ reduced to MnO_2* expressed in $\frac{1}{100}$ milligram molecules. It will be noted that originally 1 milligram molecule of $KMnO_4$ was present.
>
> β. The amount of *MnO_2 precipitated*, expressed in $\frac{1}{100}$ milligram molecules.
>
> γ. The *loss of "active oxygen"* in $\frac{1}{100}$ milligram atoms. Originally 2·5 milligram atoms of active oxygen were present.

Another column has been added, giving the number of *oxygen atoms abstracted* from the solution *per molecule of sugar* employed.

According to the equation each molecule of sugar should require twenty-four atoms of oxygen for its complete oxidation to CO_2.

Results of Experiments.

Comparatively strong solutions containing $\frac{N}{2\cdot5}KMnO_4$ and $\frac{N}{10}$ sugar with large excess of H_2SO_4 (100 molecules of $KMnO_4$ being present to 1, 2, 4 and 6 molecules of sugar in different experiments) were left stand over night.

The results obtained were complicated and in every case far too much $KMnO_4$ was reduced. This was evidently the result of some secondary action, probably the reduction of $KMnO_4$ by the MnO_2.

Consequently I decided to restrict myself to the use of dilute solutions, viz., $\frac{N}{50}KMnO_4$ (containing 3·1638 grams per litre) and $\frac{N}{500}$ sugar (containing ·6843 grams per litre).

(i.) *Experiments at ordinary temperature* (21°C.).

Solutions were made up as indicated in table on Friday afternoon and allowed to stand until the following Monday morning, *i.e.*, 64-68 hours. The solutions were then diluted to 100ccs. and sufficient filtered into a burette to titrate against either 10 or 20ccs. $\frac{N}{50}$ [Fe.]

The results shew that the reaction is not complete after three days' contact at this temperature.

Table I.

Time of experiment, 64-68hrs. Temperature 21°C.

50ccs. $\frac{N}{50}KMnO_4$ and 5ccs. $\frac{N}{2}H_2SO_4$ were employed in each experiment.

No. of Experiment.	Sugar Employed.	Ferrous Solution used.	Result of titration.	$KMnO_4$ reduced to MnO_2 (a)	Oxygen atoms abstracted per molecule of Sugar.
1	5ccs. $\frac{N}{500}$	20ccs. $\frac{N}{50}$	9·3ccs.	13·8	20·7
2	10 ,,	,,	11·3 ,,	29·2	21·9
3	15 ,,	,,	14·2 ,,	43·65	21·8
4	25 ,,	10ccs. $\frac{N}{50}$	13·5 ,,	71·35	21·4

(ii.) *Experiments at 50°–60°C.*

A solution was made up containing 15 molecules of $KMnO_4$ to 1 of sugar, and placed in a flask immersed in water heated to 50°–60°. All the $KMnO_4$ has not been reduced to MnO_2 at the end of $2\frac{1}{2}$ hours.

The temperature was then raised to 80° and the remaining colour disappeared in less than 20 minutes.

As the action was so slow at 50°–60°, further experiments were not attempted at this temperature.

(iii.) *Experiments at temperatures above 80°C.*

From 80° to 90° has appeared to be the most convenient temperature, for if colder the action is too slow, and if hotter, then the secondary action has an appreciable influence on the result.

It will be seen from the table of results, that the reaction at this temperature is practically complete in 1 hour under these conditions of experiment. Experiment 4 is apparently incorrect. The high values in Experiments 9, 10 and 11 are apparently due to the secondary action being accelerated by the higher temperature. The action is evidently not largely affected by the quantity of acid present, when within moderate limits; see Experiments 2, 3 and 7.

TABLE II.

50ccs. $\frac{N}{50}KMnO_4$ was employed in every case.

The amount of sugar was arranged so that the ratio of sugar molecules to $KMnO_4$ molecules originally present varied from 1%–5%.

No. of Experiment.	Time in Hours.	Temperature of Experiment.	ccs. of $\frac{N}{2}$ Acid used.	ccs. of $\frac{N}{500}$ Sugar used.	Per cent.	$KMnO_4$ reduced to MnO_2 (α)	Oxygen atoms abstracted per molecule of Sugar.
1	$1\frac{1}{4}$	80°	10ccs.	10ccs.	2	30·56	22·92
2	1	80°–90°	0·75	20	4	64·6	24·23
3	1	,,	2·0	20	4	64·52	24·2
4	1	,,	5·0	10	2	28·66	21·5
5	1	,,	,,	15	3	48·4	24·2
6	$1\frac{1}{2}$	,,	,,	15	3	48·06	24·03
7	1	,,	,,	20	4	62·12	23·24
8	1	,,	,,	25	5	79·65	23·90
9	2	80°–95°	,,	5	1	17·23	25·84
10	2	,,	,,	10	2	34·96	26·22
11	$1\frac{1}{2}$	,,	,,	10	2	32·84	24·63

It was thought advisable to determine the influence, if any, of both much larger and smaller quantities of acid, as the action may possibly be considerably influenced thereby.

The results obtained shewed that when no acid was present, comparatively little action takes place, but as long as sufficient acid is present to combine with the potassium of the reduced $KMnO_4$, only a slight effect is produced by even increasing the acid sixty-fold. (See Experiments 2, 3 and 4 in Table III.).

TABLE III.

50ccs.$\frac{N}{50}$ $KMnO_4$ and 15ccs.$\frac{N}{500}$ sugar were employed in every case.

No. of Experiment.	Time in Hours.	Temperature of Experiment.	ccs. of $\frac{N}{2}$ acid employed.	$KMnO_4$ reduced to MnO_2 (a)	Oxygen atoms abstracted per molecule of Sugar.
1	1	(82°) 79°·5–84°·5	none	19·6	9·8
2	1	(80°) 75°–85°	0·5 ccs.	45·4	22·7
3	1	(82°) 79·5–84·5	1·0 ccs.	46·4	23·2
4	1	(80°) 75–85	30 ccs.	47·4	23·7
5	1¼	(85) 84–86	·5 ccs.	46·8	23·4
6	1¼	(83) 84–86	30 ccs.	48·4	24·2

The effect of a still higher temperature remained to be investigated, and with this object experiments were undertaken at the boiling point (101°C.).

Table IV. clearly shows that while 24 atoms of oxygen to each molecule of sugar had been abstracted from the solution in the first 30 minutes, yet the secondary action had attained to such importance that no less than 14% of the remaining $KMnO_4$ was reduced to MnO_2 in the following 30 minutes.

Sufficient sulphuric acid was present to combine with the potassium of all the $KMnO_4$ employed.

TABLE IV.

50ccs.$\frac{N}{50}$KMnO$_4$, 15ccs.$\frac{N}{500}$sugar and 1cc.$\frac{N}{2}$H$_2$SO$_4$ were employed in each experiment.

No. of Experiment.	Time in Minutes.	Temperature of Experiment.	KMnO$_4$ reduced to MnO$_2$ (a)	Oxygen atoms abstracted per molecule of Sugar.
1	15	101°C	46·05	23·02
2	30	,,	48·16	24·08
3	45	,,	50·25	25·12
4	60	,,	55·0	27·5

The question arises as to whether the reduction of the KMnO$_4$ will continue even after all the sugar can reasonably be assumed to have been oxidised. According to Morse and Reese (*loc. cit.*) the action should not stop until all the KMnO$_4$ has been decolorized, and even then the MnO$_2$ itself should begin to lose oxygen.

My experiments (Table V.) bear out this view as far as they go.

In Experiment 1 no organic reducing agent was present.

TABLE V.

50ccs.$\frac{N}{50}$KMnO$_4$ were employed in each experiment.

No. of Expt.	Time in Hours.	Temperature of Experiment.	ccs. of $\frac{N}{500}$ Sugar used.	Per cent.	ccs. of $\frac{N}{2}$ H$_2$SO$_4$	KMnO$_4$ reduced to MnO$_2$ (a)	Loss of "Active Oxygen" (γ)	Oxygen atoms abstracted per molecule of Sugar.
1	$4\frac{1}{4}$	(94°) 92°–96°	none		25 ccs.		22·4	
2	$3\frac{1}{2}$	(95°) 93°–98°	15	3	·66	51·9		26·0
3	$3\frac{1}{2}$	(95°) 93°–98°	15	3	30 ccs.	57·9		29·0
4	$4\frac{1}{4}$	(94°) 92°–95°	10	2	·66	35·0		26·2
5	$4\frac{1}{4}$	(94°) 92°–95°	10	2	30 ccs.	43·1		32·3
6	4	(94°) 92°–96°	10	2	30 ccs.	45·3		34·0

As in all these series of experiments, the presence of the acid exercises a notable effect, it was thought advisable to determine the amount of reduction undergone by an ordinary standard solution of $KMnO_4$ when heated with varying amounts of dilute H_2SO_4 at different temperatures.

The amount of reduction was estimated by titration against [Fe.] Solution.

TABLE VI.

No sugar was employed in these experiments.

No. of Experiment.	Temperature of Experiment.	Time in Hours.	$\frac{N}{50} KMnO_4$ employed.	$\frac{N}{2} H_2 SO_4$ present.	Percentage loss of "active oxygen" of $KMnO_4$ solution.
1	101°C.	1	50ccs	5ccs.	1·25%
2	,,	1	25ccs.	15ccs.	2·25%
3	94°C.	1	50ccs.	10ccs.	·4 %
4	,,	2	,,	10ccs.	1·65%
5	,,	1	,,	20ccs.	·4 %
6	,,	4¼	,,	25ccs.	9·0 %
7	,,	1	,,	30ccs.	1·0 %
8	80°C.	4	25ccs.	0ccs.	·37%
9	,,	4	,,	5ccs.	1·9 %
10	,,	4	,,	25ccs.	2·1 %

It seemed possible that a method based on this reaction might be worked out for the estimation of cane sugar in dilute solutions somewhat on the lines of the Forchammer process, which is used for the detection and estimation of organic matter in potable and other waters.

It will of course be necessary to make a correction for the secondary action or to render it inappreciable.

Several series of experiments have been carefully performed with the object of measuring the velocity of the reaction at different temperatures : these will indicate (*a*) the time required for the theoretical amount of $KMnO_4$ to be reduced, (*b*) the effect due to the secondary action on continuing the experiment beyond that time.

It should be possible from the laws of mass action to calculate the amount of $KMnO_4$ reduced in any given time.

Table VII.

Velocity of the reaction at 101°C.

50ccs.$\frac{N}{50}$KMnO$_4$, 15ccs.$\frac{N}{500}$ sugar and 1cc.$\frac{N}{2}$H$_2$SO$_4$ were used in every case, except Experiment 8.

No. of Experiment.	Time in Minutes.	KMnO$_4$ reduced to MnO$_2$ (a)	Amount of MnO$_2$ precipitated (β)	Oxygen atoms abstracted per molecule of Sugar (average value)
1	5	38·8	40·4	19·8
2	10	45·6	45·95	22·9
3	15	46·8	47·2	23·5
4	20	47·9	48·1	24·0
5	30 {	49·7	}	25·1
6		50·3	50·7 }	
7	40	51·3	51·4	25·65
8*	20	49·3	49·2	24·65

* In Experiment 8, 5ccs.$\frac{N}{2}$H$_2$SO$_4$ were employed.   (Compare with Experiment 4).

Table VIII.

Velocity of the reaction at 94°C.

50ccs.$\frac{N}{50}$KMnO$_4$, 15ccs.$\frac{N}{500}$sugar and 1cc.$\frac{N}{2}$H$_2$SO$_4$ were used in every case.

No. of Experiment.	Time in Minutes.	KMnN$_4$ reduced to MnO$_2$ (a)	MnO$_2$ precipitated (β)	Loss of "active oxygen." (γ)	Oxygen atoms abstracted per molecule of Sugar (average value).
1	10			55·75	18·58
2	20	45·18	45·3		22·62
3	30	47·25	47·25		23·62
4	35 {	48·09			24·05 }
5				71·4	23·80 }
6	40	48·81	48·80		24·4
7*	45	48·81	49·0		24·45
8	60	49·87	49·8		24·93
9	80			75·4	25·13
10	90	50·67			25·33

* The temperature of Experiment 7 was about 0·5°C. lower than Experiment 6, hence the closeness of the results.

TABLE IX.

Velocity of the reaction at 84·5°C.

50ccs. $\frac{N}{50}$ KMnO$_4$, 15ccs. $\frac{N}{500}$ sugar and 1cc. $\frac{N}{2}$ H$_2$SO$_4$ were used in every case.

No. of Experiment.	Time in Minutes.	KMnO₄ reduced to MnO₂ (a)	MnO₂ precipitated. (β)	Loss of "active oxygen." (γ)	Oxygen atoms abstracted per molecule of Sugar (average).
1	10			35·75	11·92
2	20			60·75	20·25
3	40	44·44	43·15		22·83 }
4				69·60	23·2 }
5	60	47·58	47·5		23·83
6	80			73·65	24·55 }
7		48·85	48·75		24·47 }
8*	120	49·95	48·9		25·32

* The temperature of Experiment 8 was 85°C.

It will be seen that at 101°C. the action reaches its theoretical limit in 20 minutes, but the secondary action is so appreciable that an error of 1 per cent. would be produced by allowing the action to continue for one minute longer. At 94°C., about 35 minutes are required, and at 84·5°C., about 65 minutes, but in these cases an error of two or three minutes is insignificant.

It was now necessary to vary the amount of sugar present, for in these three series of experiments, 15ccs. of $\frac{N}{500}$ sugar solution had been employed in each case.

The following experiments show that under the conditions of experiment the amount of action is considerably influenced by the volume of the solution, and in this particular case the number of oxygen atoms "abstracted" per molecule of sugar varies inversely as the square root of the volume, approximately. This is evidently an empirical relation only.

TABLE X.

Influence of varying the sugar present.

50ccs. $\frac{N}{50}$ KMnO$_4$ and 1cc. $\frac{N}{2}$ H$_2$SO$_4$ were employed in each case.

Duration of Experiment, 30 minutes.   Temperature, 94°C.

No. of Experiment.	ccs. of $\frac{N}{500}$ Sugar used.	Total volume of Liquid.	KMnO$_4$ reduced to MnO$_2$ (α)	MnO$_2$ precipitated. (β)	Loss of "active oxygen."	Oxygen atoms abstracted per molecule of Sugar (average).
1	5	56ccs.	16·7	17·0		25·27
2*	15	66ccs.	47·25	47·25		23·62
3	25	76ccs.			111·25	22·25

* This experiment has been given before in Table VIII.

It was evident that the volume must be kept constant, so another series of experiments was conducted at 85·0°C., in which, after adding the KMnO$_4$, acid and sugar and sufficient distilled water was run in to make the total volume up to 76ccs.

As diluting the solution will naturally make the action slower, the duration of each experiment was fixed at 80 minutes.

TABLE XI.

Influence of varying the amount of sugar present.

50ccs. $\frac{N}{50}$ KMnO$_4$ and 1cc. $\frac{N}{2}$ H$_2$SO$_4$ were employed in every case.

Duration of Experiment, 80 minutes.   Temperature, 85°C.

No. of Experiment.	ccs. of $\frac{N}{500}$ Sugar present.	Per cent.	Total loss of "active oxygen." (γ)	Excess over the theoretical limit.	Oxygen atoms abstracted per molecule of Sugar.
1	none		0·25	0·25	—
2	0·5ccs.	0·1	3·6	1·2	35·0
3			24·6	·6	
4	5	1	24·6	·6	24·7
5			24·95	·95	
6	10	2	49·2	1·2	24·6
7	15	3	72·25	·25	24·08
8	20	4	93·5	−2·5	23·4
9	25	5	111·65	−8·35	22·33

It will be seen that the reduction in Experiment 1 was only equivalent to 1 part in 1000, an amount only just recognizable by volumetric methods, whilst in Experiment 2, a comparatively large reduction has been effected by the formation of an appreciable, though small, amount of MnO_2.

The accompanying plate shews that the curve, representing the amount of action, at first runs just above and parallel to the theoretical line until after passing the 3% mark, when it crosses the line and suddenly bends downwards.

The amount of sugar contained in 25ccs. of an aqueous solution may be easily estimated in this way, provided that between 1% and 3% of a milligram-molecule is present, a small correction being made for the secondary action.

But outside these limits the process, in its present form, is not susceptible of much accuracy.

Three methods of overcoming the difficulty have presented themselves (a) by increasing the duration of each experiment to, say, two hours. This was tried, but the results obtained were unsatisfactory. (b) it was suggested that perhaps the sucrose would not itself reduce the $KMnO_4$, but would only do so after inversion, as in the case of "Fehlings" solution, and that consequently, if this were so, previous inversion of the sugar solution should considerably increase the velocity of the reaction. This was also tested by experiment, but without any notable result. (c) by increasing the amount of acid to 5ccs. or 10ccs. of $\frac{N}{2}$ H_2SO_4 and if not too tedious, working at a lower temperature in order to minimise the secondary action.
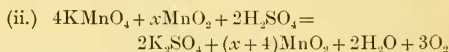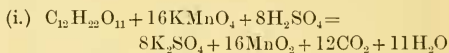
It is my intention to pursue this method further, as there is room for a process capable of more than approximately estimating the sucrose in such dilute solutions (0·3 per cent.) as we are here concerned with.

As previously intimated, it should be possible to deduce a formula which will fit the curves that have been obtained at 101°, 94° and 85°C.; of course a correction must be made for the influence of the secondary action and this, though small, is difficult to exactly determine.

I have attempted to apply the equations for mono-, di- and tri-molecular changes to the results obtained at $84°\cdot5C.$; as was to be expected they did not agree, the curve being evidently of a much higher degree and requiring a considerably more complicated equation.

The results obtained so far may, I think, be summarized as under :—

1. Cane sugar is completely oxidised to carbon dioxide and water by potassium permanganate in dilute and acid solutions containing excess of the permanganate.

2. The potassium permanganate is reduced, under these conditions, to a hydrated manganese peroxide.

3. A *secondary action* which proceeds simultaneously is caused by this precipitated oxide acting " catalytically," and reducing more of the $KMnO_4$ to MnO_2 with liberation of oxygen gas.

4. These reactions may be represented by the following equations :—

   (i.) $C_{12}H_{22}O_{11} + 16KMnO_4 + 8H_2SO_4 =$
   $$8K_2SO_4 + 16MnO_2 + 12CO_2 + 11H_2O$$

   (ii.) $4KMnO_4 + xMnO_2 + 2H_2SO_4 =$
   $$2K_2SO_4 + (x+4)MnO_2 + 2H_2O + 3O_2$$

5. The primary action indicates a method for the estimation of cane sugar in dilute aqueous solutions, bearing in mind the restrictions discussed on p. 235.

6. The velocity of both reactions increases notably, but not in a simple manner, with the concentration, acidity and temperature of the solution.

7. When excess of potassium permanganate is *not* employed, then lower oxidation products of sugar, such as formates and possibly oxalates and glycollates, are formed, as well as carbon dioxide.

These experiments have been carried out in the Chemical Laboratory of the University of Melbourne, and I desire greatfully to acknowledge my deep obligations to Professor Orme Masson for valuable encouragement and advice afforded me in connection with this work.

Duration of Experiment in minutes.